



CHARACTERIZATION OF NITROGEN-DOPED NiAl

R.D. Noebe and A. Garg
NASA Lewis Research Center, M.S. 49-3,
Cleveland, OH., 44135

(Received October 8, 1993)

Introduction

Poor tensile ductility and fracture toughness below the brittle-to-ductile transition temperature are the primary factors limiting acceptance of NiAl as a high temperature structural material [1]. Consequently, current research has been directed towards understanding the relationship between various metallurgical parameters and mechanical behavior, with emphasis on interstitial impurity effects. Interstitial elements do exert some influence on the flow behavior of single crystal NiAl. As expected, yield strength is essentially proportional to the total interstitial content of the material [2]. However, yield strength was also found to be very sensitive to substitutional alloying additions and thermal vacancies which can mask the observation of interstitial element effects [2]. Mechanistically, interstitial levels have only a marginal influence on the deformation behavior of NiAl as determined by differences in the activation volumes and stress exponents for conventional purity and high purity materials [3]. Furthermore, various annealing and prestrain treatments performed in an effort to introduce strain aging effects in NiAl resulted in absolutely no difference in these activation parameters [4]. Still, it has been suggested that interstitial impurities such as C, O and N may have a detrimental impact on the low temperature fracture behavior of NiAl, especially considering the influence that such elements have on bcc metals, i.e., strain aging embrittlement of mild steels [5]. Evidence for a similar embrittlement phenomenon in NiAl has been provided by Hack et al. [6] for NiAl single crystals containing 330-660 atomic parts per million (appm) total of C, O, and N, though the specific element(s) responsible for the embrittlement was not identified. Furthermore, George and Liu [7] have shown that an intentional carbon addition of approximately 1000 appm reduces the room temperature tensile elongation of cast plus extruded polycrystalline NiAl from just over 2 percent to essentially zero.

Nevertheless, the relationship between interstitial impurities and fracture behavior in NiAl is not completely understood. Significant work by Margevicius et al. [8-10] has demonstrated that the yield point commonly observed in polycrystalline NiAl [11,12] can be eliminated by prestraining the material by hydrostatic pressurization prior to testing. The elimination of the yield point was attributed to an increase in the mobile dislocation density. However, the yield point could be recovered by aging the prestrained material at a temperature of 673 K [13]. The flow behavior of polycrystalline NiAl due to prestrain and various thermal treatments as described by Margevicius et al. [8-11,13], is a classic example of strain aging behavior due to the pinning of dislocations by obstacles such as interstitial impurities. Yet, in contrast to the fracture toughness results on single crystals reported by Hack et al. [6] the tensile ductilities of the polycrystalline NiAl samples studied by Margevicius et al. [13] were independent of any combination of prestrain and/or thermal treatments.

Therefore, it is probably safe to conclude that interstitial elements have a definitive effect on the flow behavior of NiAl, but the relationship between interstitial elements and fracture behavior is still unclear. Furthermore, there has been little work done to identify those interstitial elements responsible for the various observations recorded in the literature. Consequently, the purpose of this note is to describe the effect of nitrogen doping on the microstructure and tensile properties of NiAl.

Experimental Procedures

A nitrogen-doped NiAl alloy was produced by Homogeneous Metals, Inc., of Troy, NY, using a conventional vacuum atomization process [14] with the exception that nitrogen gas was used instead of argon during powder production. During the vacuum atomization process the molten metal is supersaturated with gas under high pressure. When the pressurized metal is suddenly exposed to a lower pressure atmosphere (partial

vacuum) the gas expands causing the molten liquid to atomize. Usually an inert gas such as argon is used to pressurize the molten metal but in order to increase the nitrogen content in the subsequent NiAl powder material, nitrogen gas was used to charge the melt and was used as a cover gas in the atomization chamber.

The stoichiometric -100/+325 mesh prealloyed NiAl powder (Heat P1810) was placed in a mild steel extrusion can, which was evacuated and subsequently extruded at 1200 K and an area reduction ratio of 16:1. Round button-head tensile specimens were ground from the extruded rod so that the gage length of the sample was parallel to the extrusion direction. Sample dimensions were 30.5 mm and 3.1 mm for the tensile gage lengths and gage diameters, respectively. Prior to testing of the as-extruded material, all samples were electropolished in a 10% perchloric acid-90% methanol solution that was cooled to 208 K. Tensile tests were performed to failure in a universal screw-driven load frame at a constant crosshead velocity corresponding to an initial strain rate of $1.4 \times 10^{-4} \text{ s}^{-1}$. Tests were performed in air between 300 and 700 K by heating the samples in a 3-zone resistance furnace. The temperature gradient along the tensile gage section was held within $\pm 2 \text{ K}$ at all temperatures. True stress-plastic strain data were calculated from the load-time plots by accounting for the elastic strain and machine compliance and assuming constant volume conditions and uniform deformation. Yield stress values were determined by the 0.2% offset method.

Microstructural characterization of the as-extruded material and selected tensile samples was performed in a Phillips 400T transmission electron microscope (TEM) operating at 120 kV. Specimens for TEM observation were prepared by electrochemical polishing of thin slices cut from the as-extruded rod or gage sections of tested tensile specimens. Samples were prepared in a twin-jet Tenupol-3 polisher using a solution of 70% ethanol, 14% distilled water, 10% butylcellosolve, and 6% perchloric acid cooled to 263 K. An applied potential of 20-25 V with a corresponding current of 10-15 mA produced electron transparent foils.

TABLE I
Interstitial Content of N-Doped NiAl and Typical Polycrystalline NiAl Alloys
(atomic percent analysis)

Material	Carbon	Oxygen	Nitrogen	Comments
PM-NiAl(N) P1810	0.0057	0.0347	0.0904	Vacuum atomized NiAl powder using nitrogen gas followed by extrusion.
PM-NiAl P541 (Ref. 15) P1418	0.0110 0.0143	0.0170 0.0227	0.0009 0.0006	Vacuum atomized NiAl powder using argon gas followed by extrusion.
CE-NiAl L2692 (Ref. 16)	0.0114	0.0074	0.0006	Induction melted ingot followed by extrusion.

Results

Microstructural Characterization: Interstitial analysis of the as-extruded, nitrogen-doped material, designated PM-NiAl(N), is shown in Table I. For comparison purposes, Table I also contains interstitial contents for two different binary NiAl alloys produced by the same powder metallurgy route as described in the experimental section except that argon gas was used instead of nitrogen gas during powder production [15]. These binary powder metallurgy alloys are designated as PM-NiAl and can be further identified by the respective heat number, either P541 or P1418. Table I also contains the interstitial analysis of a typical cast plus extruded NiAl alloy [16], CE-NiAl. The oxygen content in the PM-NiAl(N) alloy is higher than the other three materials while the carbon level is about half of that measured in the other NiAl alloys. However, the main difference between these materials is the nitrogen content. The nitrogen-doped NiAl contains at least two orders of magnitude higher level of nitrogen than the conventional polycrystalline alloys listed in Table I.

The as-extruded microstructure of the nitrogen-doped alloy consisted predominantly of fine (2-6 μm) equiaxed grains containing a "recovered" structure composed of dislocation networks and subgrain boundaries, Fig. 1. Semi-continuous stringers of very fine nanometer size precipitates were observed primarily along some of the grain boundaries as indicated by the arrows in Fig. 2. Because not all the boundaries contained these stringers they probably represent prior particle boundaries from the original powder particles. Energy



Fig. 1. Microstructure of as-extruded PM-NiAl(N) consisting of equiaxed grains containing dislocation networks and subgrain boundaries.

Fig. 2. AlN precipitates (marked "A") and prior particle boundaries (indicated by the arrows) in as-extruded PM-NiAl(N).



Fig. 3. Hexagonal shaped AlN precipitate and its corresponding [0001] axis microdiffraction pattern.

dispersive spectroscopic analysis of the stringers indicated that the particles were rich in Al and N but also contained some O. Individual particles that made up the stringers were too fine to analyze by selected area diffraction (SAD) but are probably precipitates of AlN [17] or an aluminum oxy-nitride. Occasionally, larger precipitates, several hundred nanometers in size, were observed within individual grains. These precipitates were faceted or hexagonal in shape and are marked "A" in Fig. 2. Analysis of microdiffraction patterns taken from the particles indicated that they were AlN precipitates, Fig. 3. Therefore, the majority of the nitrogen was not in solution and instead was present in the form of second phase particles.

Tensile Properties: Typical room temperature true stress-plastic strain curves for the PM-NiAl(N) alloy, the two binary NiAl alloys produced by conventional powder processing, and CE-NiAl, are shown in Fig. 4. All alloys represented in Fig. 4 were produced by extrusion at nominally 1200 K and an area reduction ratio of 16:1 and were tested at room temperature in the as-extruded condition. The two binary PM-NiAl alloys represent samples from two different heats of powder and display roughly the same behavior. The three binary NiAl alloys exhibited discontinuous yield behavior. Both PM-NiAl alloys displayed a pronounced yield point and Luders strain while the CE-NiAl alloy exhibited a slight yield point and small Luders strain or region of low work hardening rate. Similar tensile stress-strain curves have been previously reported for binary NiAl alloys [8-13,16]. In contrast, the nitrogen-doped alloy exhibited a continuous and smooth yield behavior with no sign of a yield point or any discontinuous flow behavior. Even more unusual was how the yield strength of the various alloys compared. The strength level of the PM-NiAl(N) alloy was between that of the binary PM-NiAl and CE-NiAl. The higher yield strength of the PM-NiAl alloy from Heat P541 could possibly be due to a difference in stoichiometry since the alloy was Al rich by almost a half of an atomic percent [15]. However, the remaining three alloys were stoichiometric and similar in composition within experimental accuracy (± 0.2 at.%). The room temperature tensile elongation of the nitrogen-doped alloy ranged from about 1.5 to 3% and on average was higher than any of the NiAl alloys previously produced at NASA LeRC.

The dislocation structure in a tensile sample of PM-NiAl(N) deformed to about 2% plastic strain at room temperature is shown in Fig. 5. Even after this relatively small strain, the dislocations have begun to organize into a cell structure. This type of dislocation structure has been observed in previous studies of deformed near stoichiometric NiAl alloys [15,18] and is indicative of very easy cross-slip within the NiAl grains.

The temperature dependent tensile properties (0.2% offset yield stress, fracture stress and tensile elongation) for the PM-NiAl(N) alloy are summarized in Fig. 6. The temperature dependent tensile behavior of the nitrogen-doped alloy was very similar to the binary cast plus extruded material [16] and fine grained powder processed NiAl [19]. The yield strength decreased slightly with increasing temperature, while the fracture strength and tensile elongation increased very dramatically just above room temperature. The brittle-to-ductile transition temperature (BDTT) for this material was between 500 and 550 K making it as low as any transition temperature reported for NiAl [20]. Consequently, there is no indication that nitrogen has any embrittling effect on NiAl. In fact, nitrogen is about the only alloying addition presently known that does not increase the BDTT of polycrystalline NiAl [16,20].

Discussion

It is apparent from this study that the solubility for nitrogen and oxygen in NiAl is low, as evident from the presence of oxide and nitride precipitates. The tensile tests indicate that these interstitial elements at levels in excess of their solubility limit appear to have absolutely no detrimental effect on the properties of NiAl. In fact, the room temperature tensile ductility is as good, and the BDTT is as low, as that reported for any polycrystalline NiAl alloys. The presence of nitrogen also did not affect the slip behavior of NiAl. Cross-slip was just as prominent in the doped alloy as in binary NiAl. Even though the doped alloy has a total interstitial content of approximately 1300 appm compared to 300-400 appm for conventional purity materials, there was no indication of a yield point phenomenon in this material that would be indicative of dislocation-interstitial interactions. Also, the yield stress was significantly lower for the PM-NiAl(N) alloy than for similarly produced binary PM-NiAl alloys. However, all three PM-alloys had yield stresses substantially higher than that for the cast plus extruded NiAl. The reason for the high yield stress for powder metallurgy processed material is presently under investigation.

In a study by George and Liu [7], carbon was added to NiAl in the same level as nitrogen added to NiAl in this study. However, carbon seems to embrittle NiAl [7]. In α -Fe, both nitrogen and carbon tend to have similar effects on properties resulting in various strain aging phenomena [5]. Therefore, it was surprising that nitrogen was not detrimental to the mechanical properties of NiAl. This can partly be explained by the very low solubility of nitrogen in NiAl. It is also possible that the lower level of carbon in the nitrogen-doped alloy may be partly responsible for the good mechanical properties exhibited by this material and the lack of a yield point

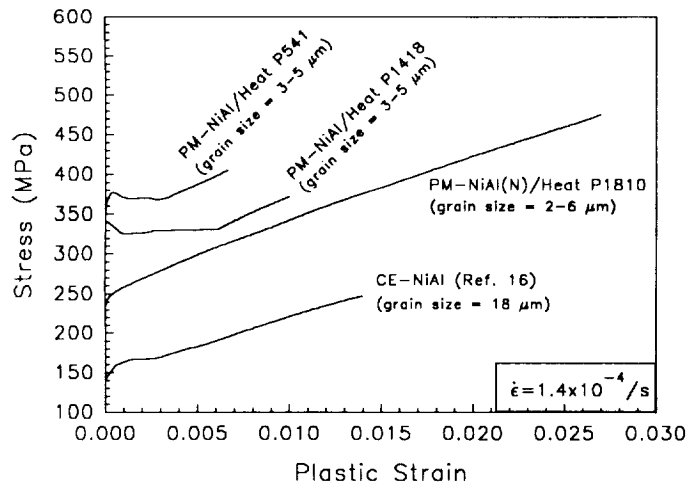


Fig. 4. Room temperature stress-strain response for as-extruded NiAl alloys and PM-NiAl(N). Interstitial levels for all alloys are reported in Table I.

Fig. 5. Dislocation morphology in the PM-NiAl(N) alloy deformed in tension at room temperature to approximately 2% plastic strain.

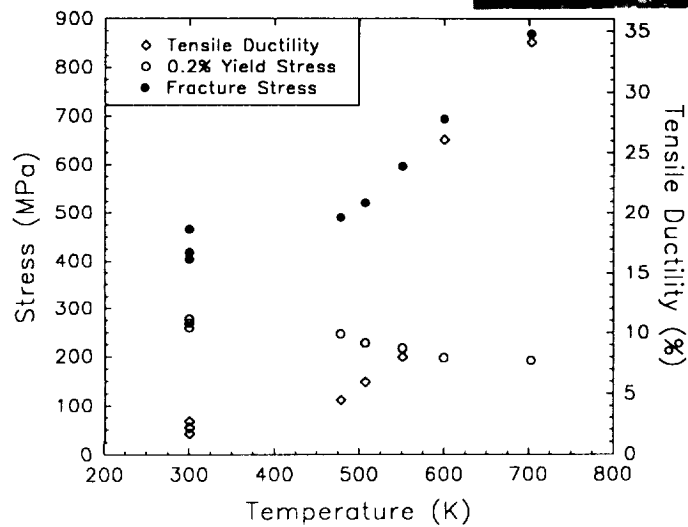
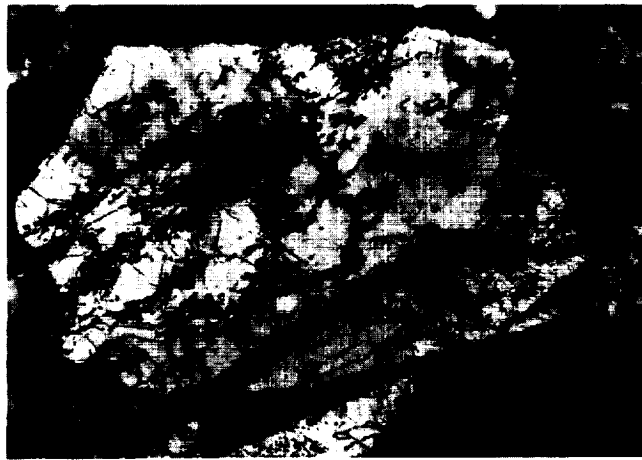


Fig. 6. Temperature dependence of the 0.2% offset yield stress, fracture stress and tensile elongation for nitrogen-doped NiAl.

in room temperature tensile tests. However, it is apparent that interstitial effects in NiAl are a very complicated issue and additional testing of materials with controlled interstitial levels will be needed. The effect of carbon on properties should be an area of particular interest and concern.

Summary and Conclusions

1. The solubility for nitrogen in NiAl is well below 900 apm.
2. Nitrogen has no adverse impact on the tensile properties of NiAl, with the nitrogen containing material exhibiting above average yield strength, tensile strength, and tensile elongation compared to any other NiAl alloys.
3. The temperature dependence of the tensile properties for the nitrogen-doped alloy was similar to that of binary NiAl. The yield strength decreased mildly with temperature and the fracture stress and tensile ductility increased significantly with increasing temperature.
4. The brittle-to-ductile transition temperature for the PM-NiAl(N) alloy was between 500 and 550 K making it one of the lowest BDTT's reported for a polycrystalline NiAl alloy.

Acknowledgements

The authors would like to thank A. Tenteris-Noebe for reviewing the original manuscript. A. Garg would like to thank the National Research Council for awarding a Research Associateship to perform this work at the NASA Lewis Research Center.

References

1. R.R. Bowman and R.D. Noebe: in Superalloys 1992, S.D. Antolovich et al., The Minerals, Metals & Materials Society, Warrendale PA., 1992, pp. 341-350.
2. M.L. Weaver, M.J. Kaufman and R.D. Noebe: *Scripta Metall. Mater.*, **29**, 1113 (1993).
3. K. Kitano, T.M. Pollock and R.D. Noebe: submitted to *Scripta Metall. Mater.*, (1993).
4. K. Kitano and T.M. Pollock: in International Symposium on Structural Intermetallics, ed. R. Darolia et al., The Minerals, Metals & Materials Society, Warrendale PA., 1993, pp. 591-599.
5. W.C. Leslie: The Physical Metallurgy of Steels, McGraw-Hill Book Company, New York, NY., 1981.
6. J.E. Hack, J.M. Brzeski and R. Darolia: *Scripta Metall. Mater.*, **27**, 1259 (1992).
7. E.P. George and C.T. Liu: *J. Mater. Res.*, **5**, 754 (1990).
8. R.W. Margevicius and J.J. Lewandowski: *Scripta Metall. Mater.*, **25**, 2017 (1991).
9. R.W. Margevicius, J.J. Lewandowski and I.E. Locci: *Scripta Metall. Mater.*, **26**, 1733 (1992).
10. R.W. Margevicius and J.J. Lewandowski: *Acta Metall. Mater.*, **41**, 485 (1993).
11. A.G. Rozner and R.J. Wasilewski: *J. Inst. Metals*, **94**, 169 (1966).
12. K.H. Hahn and K. Vedula: *Scripta Metall.*, **23**, 7 (1989).
13. R.W. Margevicius, J.J. Lewandowski, I.E. Locci and R.D. Noebe: *Scripta Metall. Mater.*, **29**, 1309 (1993).
14. J.M. Wentzell: *J. Vac. Sci. Technol.*, **11**, 1035 (1974).
15. R.R. Bowman, R.D. Noebe, S.V. Raj and I.E. Locci: *Metall. Trans. A*, **23A**, 1493 (1992).
16. R.D. Noebe and M.K. Behbehani: *Scripta Metall. Mater.*, **27**, 1795 (1992).
17. B.J.M. Aikin, R.M. Dickerson, D.T. Jayne, S. Farmer and J.D. Whittenberger: accepted *Scripta Metall. Mater.*, (1993).
18. P. Nagpal and I. Baker: *J. Mater. Sci. Lett.*, **11**, 1209 (1992).
19. R.D. Noebe, R.R. Bowman, C.L. Cullers and S.V. Raj: in High Temperature Ordered Intermetallic Alloys V, L. Johnson et al. eds., Mater. Res. Soc. Symp. Proc. Vol. 213, 1991, pp. 589-596.
20. R.D. Noebe, R.R. Bowman and M.V. Nathal: *Int. Mater. Revs.*, **38**, 193 (1993).